

CLASSIFICATION
CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

CONFIDENTIAL

REPORT

50X1-HUM

CD NO.

COUNTRY USSR
SUBJECT Scientific - Chemistry, organic phosphorus compounds
HOW PUBLISHED Thrice-monthly periodical
WHERE PUBLISHED Moscow; Leningrad
DATE PUBLISHED 21 Jul 1950
LANGUAGE Russian

DATE OF INFORMATION 1950

DATE DIST. 13 Dec 1950

NO. OF PAGES 4

SUPPLEMENT TO REPORT NO.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 50 U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE Doklady Akademii Nauk SSSR, Vol LXXIII, No 3, 1950, pp 487-489.

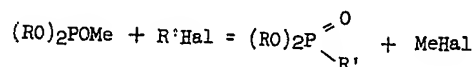
THE INTERACTION OF DIALKYLPHOSPHOROUS ACIDS
WITH ALDEHYDES AND KETONES (NEW METHOD OF SYNTHESIS
OF ESTERS OF ALPHA-HYDROXYALKYLPHOSPHONIC ACIDS)

B. S. Abramov, Kazan' Chemicotechnological
Inst imeni S. M. Kirov
Submitted by Acad A. Ye. Arbuzov
19 May 1950

[This is another paper reporting results of the extensive investigation on organic phosphorus compounds which is being carried out at several institutes in Kazan'. The work in question has CW implications, because compounds having cholinesterase inhibitor activity and products which are closely related to this class of compounds are being synthesized in the course of the investigation referred to here.]

Alpha-hydroxyalkylphosphonic acids and their derivatives have been studied little thus far, although alpha-hydroxyalkylphosphonic acids were synthesized (1-4) through the action of phosphorus trichloride or phosphorous acid on the corresponding aldehydes with the subsequent hydrolysis of products under various conditions. Hydroxymethylphosphonic acid was obtained by A. Ye. Arbuzov and N. P. Kushkova (5) in the saponification of the ester of iodomethylphosphonic acid, earlier synthesized by Page (2). Esters of alpha-hydroxyalkylphosphonic acids were first obtained by Marie (3) from silver salts of acids and alkyl iodides. Methyl and ethyl esters of alpha-hydroxyalkylphosphonic acids were obtained by M. I. Kabachnik and P. A. Rossiyskaya (6) by the reduction of esters of alpha-ketophosphonic acids with sodium amalgam in aqueous-alcoholic acetic acid solution.

The esters of alkylphosphonic acids can be obtained by various methods (7). One of the most common methods for obtaining them is the Michaelis-Becker reaction (8) -- the reaction of alkyl halides on alkaline metal salts of dialkylphosphorous acids:



- 1 -

CONFIDENTIAL

CLASSIFICATION		CONFIDENTIAL		DISTRIBUTION							
STATE	<input checked="" type="checkbox"/>	NAVY	<input checked="" type="checkbox"/>	NSRB							
ARMY	<input checked="" type="checkbox"/>	AIR	<input checked="" type="checkbox"/>	FBI							

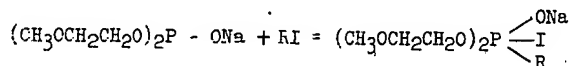
7

CONFIDENTIAL

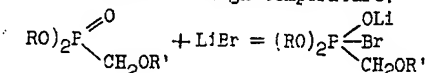
CONFIDENTIAL

50X1-HUM

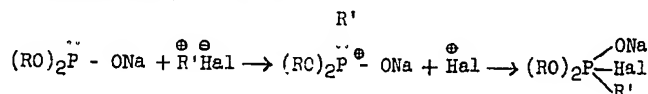
The mechanism of this reaction is considered to be either an exchange of metal for the hydrocarbon radical, if the structure of the salt is assumed to be based on pentavalent phosphorus, or as an addition of the alkyl halide to the phosphorus accompanied by the subsequent detachment of the metal halide, if the structure of the salt is assumed to be based on trivalent phosphorus. The most probable mechanism of this reaction, in our opinion, is the addition of the alkyl halide to the salts of phosphorous acid. This is confirmed, as we have shown, by the formation of products of the addition of iodides to sodium di-beta-methoxyethylphosphite in the course of the usual reaction of Michaelis-Becker,



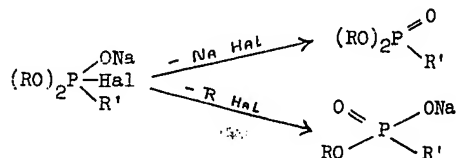
and the formation of products of addition of halogen salts of lithium (LiBr, LiI) with esters of alkoxyethylphosphonic acid as a result of the action of the lithium halide on the ester at a high temperature:



A further development of the ideas introduced into the field of organic phosphorus compounds by Academician A. Ye. Arbuzov and successfully applied by the Kazan' school of chemists under his leadership, in the explanation of the reaction of halogen compounds with salts of dialkylphosphorous acids, is the addition of the positively charged atom of carbon from the alkyl halide to the phosphorus, the latter carrying an isolated pair of electrons. This reaction scheme is shown below.

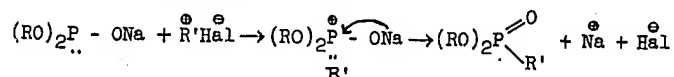


Splitting off of either sodium halide or alkyl halide follows:



The direction in which the splitting proceeds depends principally on the nature of the radical joined to the phosphorus, but also on the nature of the halide and ester radicals (intramolecular causes) and on the conditions under which the experiments are conducted.

The formation of esters of alkylphosphonic acids can be explained also by another course of the reaction:



The sodium ion and halide ion give sodium halide.

From such an explanation of the principle of the reaction, it follows that not only halogen compounds, but also other substances whose molecules are polarized similarly to those of the halogen compounds, can react with the salts of

- 2 -

CONFIDENTIAL

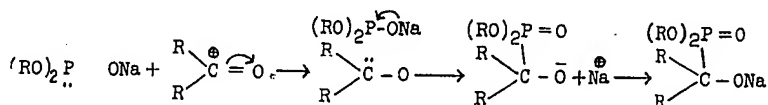
CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

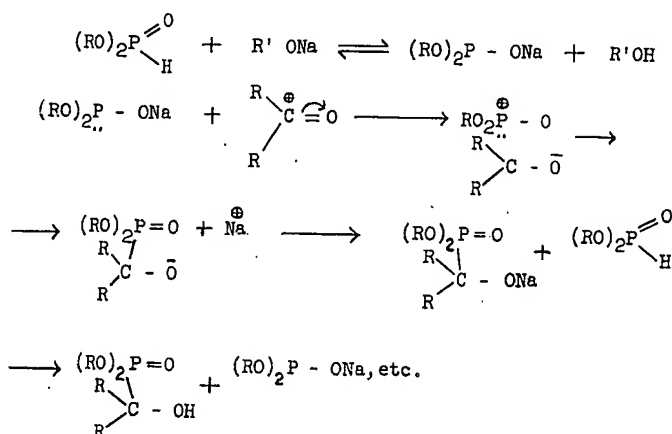
dialkylphosphorous acids. Naturally, this analogy can be extended also to cover aldehydes and ketones whose molecules are polarized. The oxygen of the carbonyl group draws electrons from the carbon-oxygen bond and makes the carbon of the carbonyl groups positively charged, i.e., capable of interaction with the isolated pair of electrons of the phosphorus in the salts of dialkylphosphorous acids:



Upon treatment of the compound thus formed with acidified water, the ester of alpha-hydroxyalkylphosphonic acid is obtained.

The addition of sodium diethylphosphite to the carbonyl group of alpha-ketophosphonic acids was first suggested by A. Ye. Arbuzov and M. M. Azanovskaya (9) in explaining the reaction of acetyl chloride on sodium diethylphosphite.

Arbuzov and A. N. Pudovik (10) showed that dialkylphosphorous acids are added to an ethylene bond which is activated by a nitrile, carbonyl, or carboxyl group in the presence of sodium alcoholate. The method indicated by us was applied to the reactions of aldehydes and ketones on dialkylphosphorous acids. Alcoholates of alkaline metals, enolating the dialkylphosphorous acid, enable this reaction to take place. In practice in experiments several drops of lithium or sodium methylate are usually employed. The reaction is expressed by the scheme:



The chain reaction progresses rapidly, generating a great amount of heat and giving a very good yield. The degree of completeness of the reaction depends on the radicals of the carbonyl group: if the radicals strengthen the effect of polarization of the molecules, then the reaction proceeds vigorously, resulting almost in a quantitative yield (for example, in the case of benzaldehyde); if, on the other hand, the radicals reduce the effect of polarization of the molecules, then the reaction proceeds at a moderate speed and the yield is correspondingly lowered. We obtained methyl, ethyl, and isopropyl esters of alpha-hydroxymethyl-, ethyl, isopropyl-, butyl-, benzyl-, cyclopentyl-, cyclohexyl-, and other phosphonic acids -- in all, more than 30 new substances. The products obtained were crystalline substances with well developed crystalline forms or thick viscous liquids.

- 3 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

Esters of alpha-hydroxyalkylphosphonic acids can be subjected to further transformations: elimination of water produces unsaturated alkylphosphonic acids, and the substitution of a hydrocarbon radical for an atom of hydrogen in the hydroxyl group produces esters of alpha-alkoxyalkylphosphonic acids.

BIBLIOGRAPHY

1. W. Fosseck, Monot., 7, 20 (1886).
2. H. J. Page, Journ Chem Soc., 101, 423 (1912).
3. Marie, C. R., 135, 1118 (1902).
4. S. B. Conant and A. O. MacDonald, Journ Am Chem Soc., 42, 2337 (1920).
5. A. Ye. Arbuzov and N. P. Kushkova, Zh. O. Kh., 6, 283 (1935).
6. M. I. Kabachnik and P. A. Rossiyskaya, Izv AN SSSR, OKI N, 364 (1945).
7. A. Ye. Arbuzov, On the Structure of Phosphorous Acid and Its Derivatives, Dissertation, 1905.
8. Michaelis u. Becker, Berlin, 30, 1003 (1897).
9. A. Ye. Arbuzov and M. M. Azanovskaya, DAN, 58, 1961 (1947).
10. B. A. Arbuzov and A. N. Pudovik, DAN, No 3 (1950).

- E N D -

- 4 -

CONFIDENTIAL

CONFIDENTIAL